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Investigation of iron ore cements

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INVESTIGATION OF IRON ORE CEMENTS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arthur Edwards Williams

ENTITLED *Investigations of Iron Ore Cements*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Science in Ceramics*

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Iron Ore Cement.

The reason for the disintegration of Portland Cement in sea water and a cure for this evil has been the cause of much discussion in the past ten years. The solution of this problem may be accredited to Mr. William Michaelis[2], who first made and tested Iron Ore Cement.

Iron Ore Cement is not manufactured in the United States at the present time and is only made by one company in Europe, "The Portland Cement Company, Hemmoor, Hamburg, Germany", under the name of Erzcement. According to Mr. William Michaelis, Jr., the process of manufacture is similar to that of Portland Cement except that limestone and iron ore are used in place of limestone and clay. United States Consular Thackara[3] gives a better description of its manufacture as follows: chalk, flintstone, and finely ground ferric oxide are used. The flint and iron are ground together then mixed with the chalk and water and screened through a fine sieve. The screened product is clinkered in a rotary kiln and then ground. An average composition of iron ore cement, given by Michaelis is:

CaO.......... 63.5%	Al_2O_3.......... 1.5%
SiO_2.......... 20.5%	MgO.......... 1.5%
Fe_2O_3........ 11.0%	Alkali........ 1.0%

The injuries which Portland Cement suffers through sea water are undoubtedly due to two sources. In the first place

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[2]Eng News - Vol. 58, p. 645 - 646.
[3]United States Consular Reports, June 1908.

chemical reaction may take place between certain constituents of the cement and the salts in sea water, and, on the otherhand, the mechanical action of the waves carrying large amounts of sand, freezing, thawing, and the varying pressure of the water due to tide help to injure the cement submerged in sea water. This thesis, however, will be confined to the chemical action of sea water, for the mechanical action is of minor importance unless the cement is weakened by chemical changes.

The reactions which take place between Portland Cement and sea water are said to be of three distinct kinds; first, the action of $MgCl_2$ and $MgSO_4$ in sea water on the calcium hydrate formed during the hardening process of the cement, forming $Mg(OH)_2$, $CaCl_2$, and $CaSO_4$. Second, the action of gypsum, $CaSO_4$ formed above, upon the calcium aluminates forming calcium sulpho aluminate. Third, the crystallization of the gypsum and calcium sulpho aluminate giving an increase in volume, thus causing the distention of the mortar.

That free lime is present in set Portland Cements is well known. Lamine[2] found 32% of CaO in cement submerged in the Black Sea 15 years. Every analysis of a cement exposed to sea water shows a high percent of MgO. Vicat[3] in 1840 showed this fact clearly, a cement, which was submerged in sea water for 6 months, was analyzed. A sample, taken from the surface exposed to the sea, showed 10.4% MgO and 19.3% CaO while the interior, which was not impaired, showed 1.87% MgO and 31.33% CaO.


[2]Le Ciment 1901 - pp. 111 - 691 - 81.
[3]Iron Ore Cement - The P. C. Co. of Hemmoor, Hamburg, Germany.

A Meyer[2] states that cement continually loses strength in sea water. The $MgSO_4$ acting with the silicate of lime forms $Mg(OH)_2$ and calcium sulphate, also that the $CaSO_4$ reacts with the calcium aluminates $(Al_2O_3, x\ CaO)$ of the cement forming $Al(OH)_3 + 3\ Mg(OH)_2 + CaSO_4 + CaCl_2$.

Charles J. Potter[3] says that $MgSO_4$ is the most active constituent in sea water on cement. He found that $MgCl_2$ softens cement but shows no expansion. Potter says that it is now definitely believed that magnesium salts act on the feebly combined lime and alumina compounds which on taking up water of crystallization cause bursting of the concrete. He mixed calcined red brick clay with Portland cement clinker in proportions of 6 to 10. From this mixture brickettes were made and placed, together with Portland cement brickettes, in fresh water, sea water, and sea water to which 10% $MgSO_4$ was added. Both of these cements gained strength in fresh water. In salt water, the Portland cement brickettes began to fail after five weeks and were disintegrated after five years. These cements showed blistering after one year, which was followed by expansion and bursting. The red cement improved continually but took eight weeks to obtain the maximium strength that the Portland cement had obtained in five weeks. In the 10% solution of $MgSO_4$, the Portland cement tested 500 lbs in a month and then went back to zero in one year. The red cement began at 250 lbs and increased continually to 1015 lbs in eight years. Mr. Potter says that the chemical combination of CaO, SiO_2 , and Al_2O_3 and water is feeble
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[2]Chemisches Central Blatt - Vol. 73, p. 1369.
[3]Jour. Soc. Chem. Ind. Vol. 28.
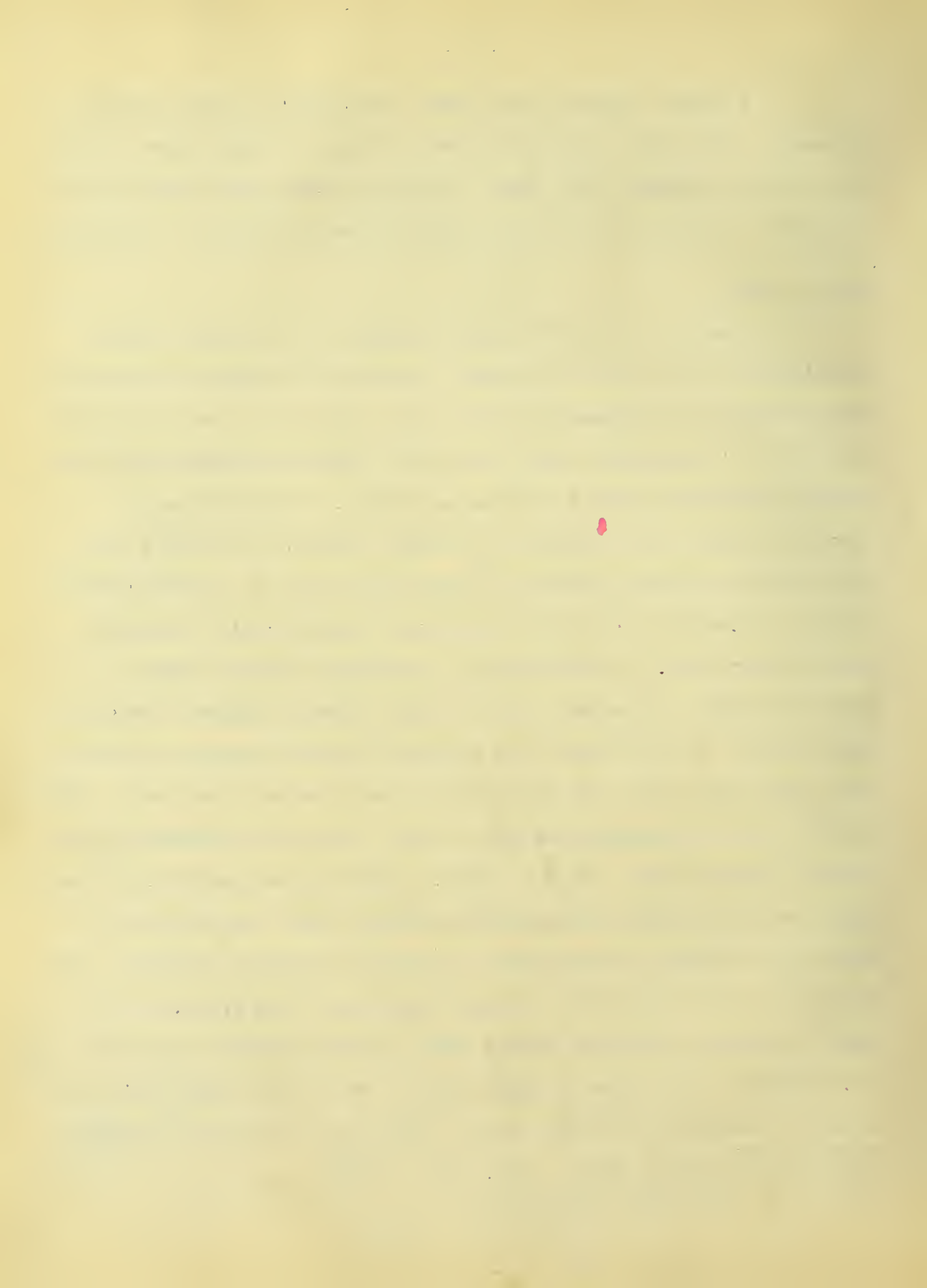
and that probably accounts for the ability of magnesium in sea water to act.

The experiments of Dr. Michaelis[2] and Le Chatelier[3] lead them to the conclusion that Portland cement suffers in solutions containing sulphuric acid salts, which applies to sea water. A double salt is formed composed of gypsum and calcium aluminate. This sulpho-aluminate, Al_2O_3, $CaO + 3CaSO_4$, is said to crystallize with thirty molecules of water which process must be accompanied by considerable expansion. Le Chatelier says that "the main cause if not the sole cause, of the injuries which cements suffer under the action of sea water is the formation of calcium sulpho-aluminate".

Rebuffat[4] says on the contrary that sulpho-aluminates cannot exist in cements in sea water but agrees with Michaelis and Le Chatelier that calcium aluminates are the parts of cement most easily acted upon by salts in sea water.

It has been shown that calcium ferrate will form similar to calcium aluminate and that alumina could be replaced by ferric oxide in Portland cement. Dr. Michaelis puts this knowledge into use with the idea of overcoming the disintegration in sea water. The result of this application is the Iron Ore Cement of to-day.

Dr. Michaelis and the Royal Experiment Station of Charlottenburg have tested these cements in comparison with Portland cements in a very thorough manner. Mr. William Michaelis[5] says in a paper read in the United States that tests of Erzcement and

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[2] Tone Industrie Zeitung - 1896 p. 838.
[3] Le Ciment 1901- p. 31 - 32.
[4] Tone Industrie Zeitung, 1901- p. 272.
[5] Eng News - Vol. 58, pp. 645 - 646.
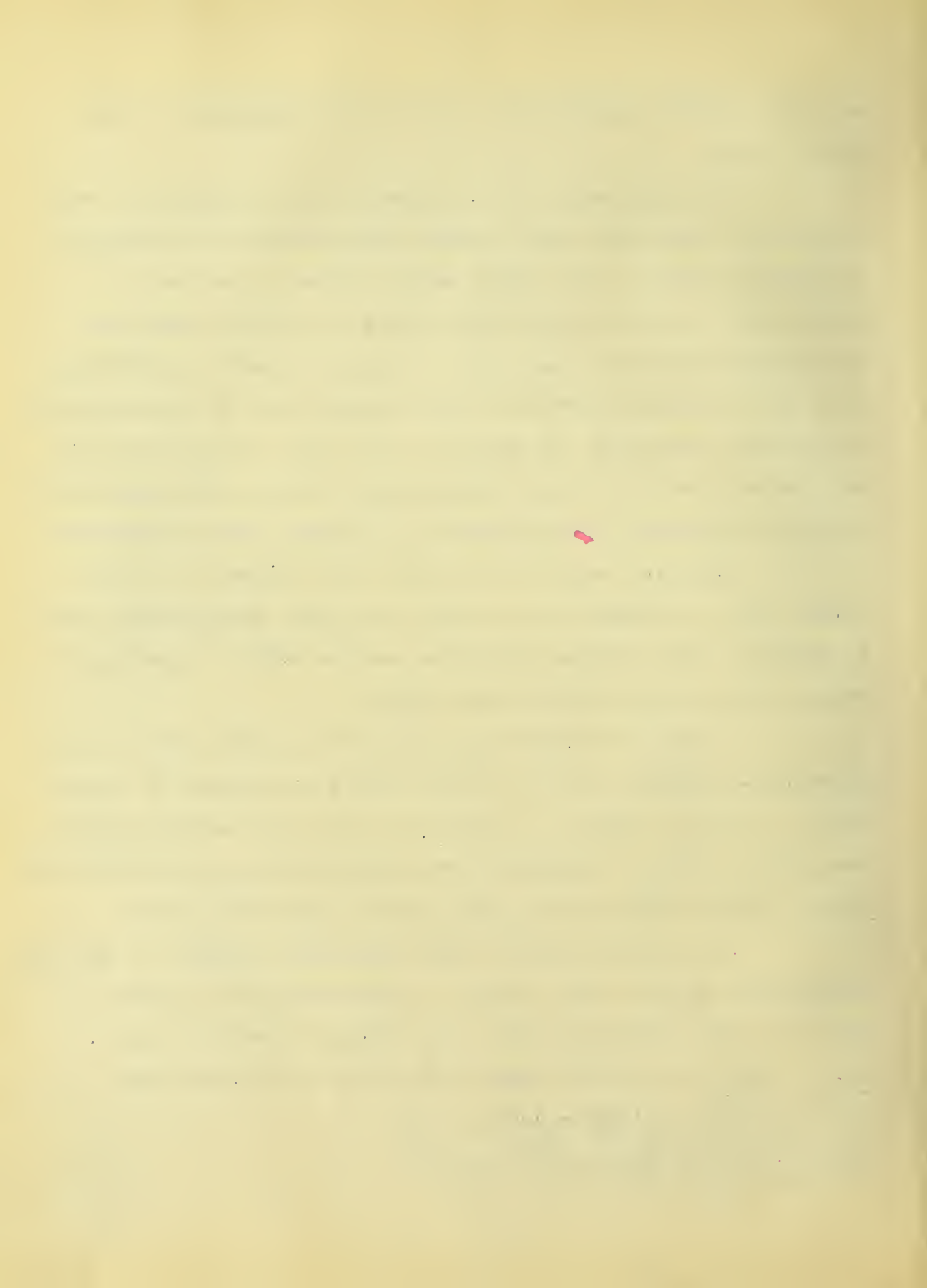
Portland were made with both neat and three to one mixtures which were placed in fresh water, sea water, and water containing fives times more salt than sea water. In sea water, the Erzcement developed a much greater strength than the Portland. In the strong salt water, the strength of the Portland cement decreased rapidly while the Erzcement showed a steady gain. Brickettes were made of Iron Ore and Portland cement which were placed in a salt solution of five times the normal strength of sea water under pressure of fifteen atmospheres for a few days. This condition destroyed the Portland cement brickettes entirely, while the Iron Ore Cement increased in strength.

The Royal Experiment Station conducted similar tests to the above but much more elaborate. Two Iron Ore and three Portland cements were made into prisms, using a three to one mixture of standard sand and cement. These prisms were placed in sea water and water containing five times the percentage of salts in ordinary sea water. In addition to this, these three solutions were allowed to act upon test pieces made of cement mixed with varied amounts of gypsum. All the Portland cement mortars disintegrated in the three and five fold salt solutions; all the Iron Ore cement mortars remained intact and sound.

United States Consul A. W. Thackara[2] investigated this cement for use on the Panama Canal. The results of his investigations was the adoption of this cement for concrete work exposed to sea water. Another point in favor of this cement is the property of slower setting. The cement is weaker than Portland for the first

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[2]United States Consular and Trade Reports - June 1908.

week, but then gradually gains strength and exceeds that of Portland.
This also allows finer grinding which gives approximately 70% to
80% active material against 30% to 40% in Portland; thus one bar-
rel of Iron Ore cement will replace three barrels of Portland.

Publications of previous experiments do not show definite-
ly the best composition for cements giving the greatest protection
against sea water. With this idea in view, the following investi-
gations were undertaken:

The outline of procedure in these experiments is as fol-
lows: Newberry's cement formula, $x(3CaO, SiO_2) + y(2CaO, Al_2O_3)$,
was used as a basis. Assuming, according to Newberry[2], that Fe_2O_3
could replace Al_2O_3 and form $2CaO, Fe_2O_3$, a triaxial diagram was
plotted (Plate I), the three members stationed at the three cor-
ners being ($3CaO$, SiO_2), ($2CaO$, Al_2O_3) and ($2CaO$, Fe_2O_3).By
blending these three members, cements could be obtained containing
various amounts of the calcium aluminate and the calcium ferrate.

The batch weights of these three members were calculated
and about 15 kilograms of each were weighed up, using practically
chemically pure materials. Whiting, flint, aluminium hydrate, and
red oxide of iron were the only ingredients. These batches were
ground in a ball mill, then passed through a 200 mesh sieve; thus
getting thorough mixing and a finely ground batch.

The following cements, No's 19, 20, 21, 22, 23, 24, 25,
36, 37, 38, 39, 40, 42, 48, 49, 50, 51, 52, 53, 54, 58, 59, 60, 61,
62, and 65 on triaxial diagram were then weighed up, blunged thor-
oughly, and partially dried by pouring the slip into plaster moulds.
The cements were then rolled into small balls about the size of a

marble, dried, and dehydrated in a down draft kiln to about 800 C and placed in fruit jars ready for burning.

These cements were burnt in a magnesite test kiln, designed by Mr. Stull of the Ceramic Department, especially for burning experimental cements. The construction of this kiln is shown in Plate II. The success of this kiln is a note worthy fact as test kilns suitable for this purpose, heretofore, have not been very satisfactory owing to lack of control, unevenness of temperature in the clinkering chamber. Kerosene oil was used for fuel with an air pressure of about 50 lbs.

The temperature at the time the clinker was drawn from the kiln was determined at first by means of a Wanner Pyrometer. This was given up, however, as the rapid rate of burning required a higher temperature than the true temperature of clinker formation.

Almost all of these cements were fused till the surface was glassy in appearance before the cement seemed well clinkered and crystals appeared. Cements No's 54, 58, 62, and 65 appeared like a Portland clinker, except darker in color and were not fused or slag like in appearance.

The clinker was first reduced in a jaw crusher and then ground in a disc mill; a screen test showed 24.2% on 150 mesh screen; 12.3% on 200 mesh screen; and the remainder 63.5% passed 200 mesh. These cements show that they are approximately of the same degree of fineness as the average Portlands. After the samples were ground, pats were made from them in the usual manner to determine the properties of the cement.

The amount of water used for mortar was determined by the

Boulonge method (Waterbury's Cement Manual - page 44). The
initial and final sets were determined with Gilmore needles.

Four pats were made of each cement with the idea of using
one for the "time of setting" tests and placing the other three
immediately in the moist closet, two of which were to be used for
the "boiling test" after 24 hours, the third to be allowed to stand
in water for 28 days. All of these cements went to pieces in cold
water or in the boiling test. The results are given in the follow-
ing table:

Formulae of Cements Made.

No		Molecular Ratio SiO_2 : $Al O + Fe_2O_3$
19	$.1(3CaO,SiO_2)+.2(2CaO,Al_2O_3)+.7(2CaO,Fe_2O_3)$	0.11
20	$.1(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.8(2CaO,Fe_2O_3)$	0.11
21	$.1(3CaO,SiO_2)+.9(2CaO, Fe_2O_3)$	0.11
22	$.2(3CaO,SiO_2)+.8(2CaO,Fe_2O_3)$	0.25
23	$.2(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.7(2CaO,Fe_2O_3)$	0.25
24	$.2(3CaO,SiO_2)+.2(2CaO,Al_2O_3)+.6(2CaO,Fe_2O_3)$	0.25
25	$.2(3CaO,SiO_2)+.3(2CaO,Al_2O_3)+.5(2CaO, Fe_2O_3)$	0.25
36	$.3(3CaO,SiO_2)+.2(2CaO,Al_2O_3)+.5(2CaO,Fe_2O_3)$	0.43
37	$.3(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.6(2CaO,Fe_2O_3)$	0.43
38	$.3(3CaO,SiO_2)+.7(2CaO,Fe_2O_3)$	0.43
39	$.4(3CaO,SiO_2)+.6(2CaO,Fe_2O_3)$	0.66
40	$.4(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.5(2CaO,Fe_2O_3)$	0.66
42	$.4(3CaO,SiO_2)+.3(2CaO,Al_2O_3)+.3(2CaO,Fe_2O_3)$	0.66
48	$.5(3CaO,SiO_2)+.3(2CaO,Al_2O_3)+.2(2CaO,Fe_2O_3)$	1.00
49	$.5(3CaO,SiO_2)+.2(2CaO,Al_2O_3)+.3(2CaO,Fe_2O_3)$	1.00
50	$.5(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.4(2CaO,Fe_2O_3)$	1.00
51	$.5(3CaO,SiO_2)+.5(2CaO,Fe_2O_3)$	1.00
52	$.6(3CaO,SiO_2)+.4(2CaO,Fe_2O_3)$	1.50
53	$.6(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.3(2CaO,Fe_2O_3)$	1.50
54	$.6(3CaO,SiO_2)+.2(2CaO,Al_2O_3)+.2(2CaO,Fe_2O_3)$	1.50
58	$.7(3CaO,SiO)+.2(2CaO,Al O)+.1(2CaO,Fe O)$	2.33
59	$.7(3CaO,SiO^2)+.1(2CaO,Al^2O^3)+.2(2CaO,Fe^2O^3)$	2.33
60	$.7(3CaO,SiO_2)+.3(2CaO,Fe_2O_3)$	2.33
61	$.8(3CaO,SiO_2)+.2(2CaO,Fe_2O_3)$	4.00
62	$.8(3CaO,SiO_2)+.1(2CaO,Al_2O_3)+.1(2CaO,Fe_2O_3)$	4.00
65	$.9(3CaO,SiO^2)+.1(2CaO,Fe_2O_3)+$	9.00

No	Time Initial Set	Time Final Set	Water Used	Remarks at time of Final Set	Conditions after 48 Hours in moist Closet.
19	1 1/2 Hr.	3 - Hr.	21.0%	Cracked in 1/2 Hr.	Cracked.
20	1 -- "	5 - "	20.0	O.K. Strong.	Warped and Cracked
21	2 1/2 "	5 1/2"	21.0	No cracks.	No Cracks.
22	1 2/3 "	4 - "	20.0	Small cracks.	No Cracks.
23	1 - "	-----	21.0	Cracked.	No Cracks.
24	3/4 "	5 1/2"	22.0	Cracked.	No Cracks.
25	1 1/4 "	-----	21.5	Cracked.	No Cracks - Soft.
36	1 3/4 "	11 -- "	20.0	Cracked.	O.K.
37	1 -- "	2 1/2"	20.0	Cracked.	No Cracks.
38	1 -- "	5 -- "	20.0	O.K.	No Cracks.
39	2.-- "	8 -- "	21.0	Cracked.	Cracked.
40	1 1/4 "	3 1/2"	20.0	Cracked.	Warped.
42	1/2 "	2 3/4	21.5	O.K.	No Cracks.
48	1 1/4 "	7 -- "	22.0	O.K.	No Cracks.
49	1 1/2 "	3 -- "	21.0	Cracked.	Cracked.
50	3 -- "	-----	22.0	Cracked.	No Cracks - Soft.
51	2 -- "	10 -- "	21.0	O.K.	Soft.
52	1 -- "	9 -- "	20.0	Soft	Soft.
53	1 1/4 "	4 -- "	21.0	Cracked.	No Cracks - O.K.
54	1 -- "	4 1/4"	23.5	Cracked.	No Cracks - O.K.
58	1 -- "	3 1/4"	22.0	No Cracks.	Cracked.
59	1/2 "	4 1/2"	21.0	O.K.	Warped.
60	1 1/2 "	5 --	21.0	Soft and Crumbly	Warped and Cracked
61	1 -- "	6 -- "	22.0	Warped.	O.K.
62	1 1/2"	-------	22.0	Did not harden.	O.K.
65	1 1/2"	-------	21.0	Cracked.	Warped.
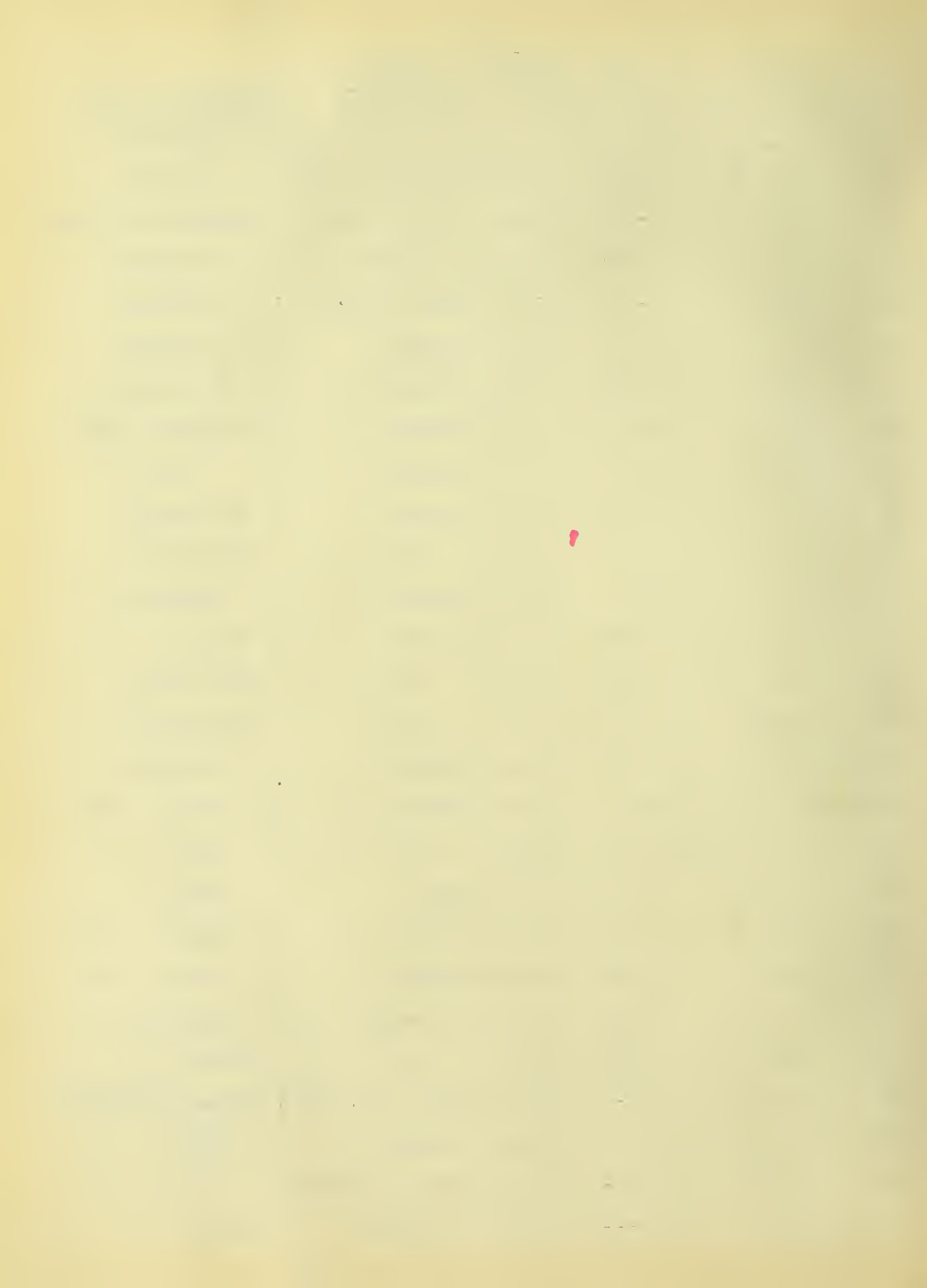
From these cements, one only, i.e. number 62 remained
sound when placed in water. This cement also stood the boiling
test (1/2 Hr), the others going to pieces. The molecular ratio of
SiO_2 to Al_2O_3 for this cement is four and since the molecular ratio
for good cements is between 5.1 and 6.8 and since none of these
cements lie between these limits, it was decided to construct a new
group. Cement number 62 approached these ratios nearer than any
other.

A new batch was calculated after Bleininger's formula
($2.8CaO, SiO_2$) + ($2CaO, Al_2O_3$) having different amounts of Fe_2O_3
and Al_2O_3 and also the ratio of SiO_2 to Al_2O_3 + Fe_2O_3 varied from
just above to just below the limits. The using of chemically pure
raw materials in place of slag and limestone gives less efficient
mixtures of lime and SiO_2. It was, therefore, thought that sufficient
lime would be obtained by the use of Bleininger's formula.

Number	Formulae
A_1	$5.1(2.8CaO, SiO_2) + (2CaO, Fe_2O_3)$
A_2	$5.8(2.8CaO, SiO_2) + (2CaO, Fe_2O_3)$
A_3	$6.4(2.8CaO, SiO_3) + (2CaO, Fe_2O_3)$
A_4	$7.0(2.8CaO, SiO_2) + (2CaO, Fe_2O_3)$
B_1	$5.25(2.8CaO, SiO_2) + 0.175(2CaO, Al_2O_3) + .825(2CaO, Fe_2O_3)$
B_2	$6.00(2.8CaO, SiO_2) + .175(2CaO, Al_2O_3) + .825(2CaO, Fe_2O_3)$
B_3	$6.40(2.8CaO, SiO_2) + .200(2CaO, Al_2O_3) + .800(2CaO, Fe_2O_3)$
B_4	$7.22(2.8CaO, SiO_2) + .175(2CaO, Al_2O_3) + .825(2CaO, Fe_2O_3)$
C_1	$5.44(2.8CaO, SiO_2) + .360(2CaO, Al_2O_3) + .640(2CaO, Fe_2O_3)$
C_2	$5.80(2.8CaO, SiO_2) + .400(2CaO, Al_2O_3) + .600(2CaO, Fe_2O_3)$
C_3	$6.40(2.8CaO, SiO_2) + .400(2CaO, Al_2O_3) + .600(2CaO, Fe_2O_3)$
C_4	$7.00(2.8CaO, SiO_2) + .400(2CaO, Al_2O_3) + .600(2CaO, Fe_2O_3)$

Percentage Composition.

No	CaO	Al_2O_3	Fe_2O_3	SiO_2	Molecular Ratio $R_2O_3 : SiO_2$
A_1	66.0	0.0	11.6	22.4	5.1
A_2	66.7	0.0	10.4	22.9	5.8
A_3	67.2	0.0	9.6	23.2	6.4
A_4	67.5	0.0	8.9	23.6	7.0
B_1	66.7	1.3	9.4	22.6	5.25
B_2	67.4	1.1	8.4	23.1	6.00
B_3	67.5	1.3	7.8	23.4	6.40
B_4	68.1	0.9	7.2	23.8	7.22
C_1	67.4	2.5	7.2	22.9	5.44
C_2	68.0	2.7	6.0	23.3	5.80
C_3	68.2	2.5	5.8	23.5	6.40
C_4	68.5	2.3	5.4	23.8	7.00

These cements were prepared in the same manner except
that the temperature of clinkering was determined as near *as* possible
by the method used. The kiln was allowed to cool to about 1000 C
before a batch of cement was put in and temperature was then grad-
ually raised till clinker was formed, the temperature was then read
with a Wanner Pyrometer.

The clinkers obtained appeared exceptionally good, being
dull black in color and glistening brightly in the sun. These
clinkers were pulverized the same as has been previously described,
then tested.

The results of these tests, given in the following table,
show that good cements can be obtained with a large amount of
Fe_2O_3 using the same ratio of SiO_2 to R_2O_3 as Portland cements
require. One very noticeable fact, however, is that when no Al_2O_3
is present as in series A_1, A_2, A_3, and A_4 that the cements all
show expansion, thus giving evidence of free lime. Although A_1
stood the boiling test, the cubes made from this cement bulged out
from the mould considerably.

The question arises at this point, is it always necessary
for Al_2O_3 to be present or can a good cement be made without it?
This ought to be possible by reducing the lime content, as A_1 was
the best of series "A" and also had the smallest amount of lime
silicate.

The slowness of setting is another factor which must be
considered. It will be seen by the table on page 14 that all of
cements required a long time to harden. This must be carried on in
a moist atmosphere also or the cement will dry out before it has
completely hydrated and set. The above factors will perhaps limit

the use of this cement to work under water which may be allowed to set a considerable time.

Results of Test.

No	Temperature when clinkered	Time to clinker	Appearance of Clinker	Initial Set	Final Set	% H_2O
A_1	1300 C	3/4 Hr	-------	24 Hrs.	62 Hr	24.8
A_2	1320	1/2 "	All.	22 "	56 "	24.0
A_3	1320	1 1/2 "	Clinkered.	26 "	56 "	23.2
A_4	1330	1/2 "	Good,	28 "	60 "	26.0
B_1	1390	1/2 "	Colored black	4 3/4	40 "	26.3
B_2	1320	1 1/4 "	and	4 1/2	44 "	24.4
B_3	1350	3/4 "	glistening	11 Hrs.	36 "	28.0
B_4	1400	1 1/2 "	with	5 "	48 "	25.0
C_1	1320	1 1/2 "	crystals	5 "	30 "	24.4
C_2	1320	3/4 "	in a	12 "	40 "	24.0
C_3	1330	1 3/4 "	bright	12 "	48 "	28.0
C_4	1380	1/2 "	light	17 "	40 "	27.2

All the cements of series "B" stood a six hour boiling test without showing any signs of expansion. In series "C" all but "C_1" stood the boiling test. "C_1" warped a little and came loose from the glass plate, although the cement has a comparatively low lime content and its formula lies between other good cements.

The attempt was next made to give these cements a comparative test with Portland cement.to show their relative resistance to sea water. The method used was similar to that of Dr. Michaelis.

Inch cubes were made of each series of cements together with a set of cubes of a standard commercial Portland cement, which had stood all the commercial tests. These were allowed to stand sixty hours in the moist chamber and then placed in water, after standing in water twenty-seven days. The cubes made from series "A" together with a set of five Portland cement cubes were placed in a steam cylinder (Plate III), containing an artificial sea water solution of ten times normal strength. The quanity of salt is shown on table page 24. The cements were then put under steam pressure of 125 lbs or 8 1/3 atmospheres, the temperature being between 150 C and 200 C. This was continued for three days. On opening the cylinder, the salt solution was found to be very dilute due to condensation of steam and no visible action on the elements had occurred. The salt solution and cubes were then put into a large wide mouthed bottle, provided with a stopper and small vent hole. The bottle was then placed inside the pressure cylinder and steam admitted, allowing little or no condensation. After being sure that the bottle was not broken by the first change in temperature, the pressure was kept on for three days longer. Upon opening the cylinder, the cubes were found bone dry and covered with salt and the bottle cracked. This was due, no doubt, to the rapid reduction of the pressure, allowing the water to vaporize rapidly, which was at a temperature above its boiling point.

The results of this test were contrary to what was expected as the Portland cements were untouched and all of the iron cements were cracked and swollen. This cracking and swelling is

caused, no doubt, by an excess of free lime, as these cements show-
ed an expansion in the boiling test and there was a deposit of
hydrated lime in the bottom of the cylinder which seemed to have
been leeched out of the cubes.

No crushing strength test of Series "A" was made as they
were all destroyed already.

Series "B" was then placed in the cylinder, with a set of
Portland cement cubes. A vessel made of 4" pipe was used in place
of the glass bottle to overcome cracking due to sudden change in
temperature. This series was kept under pressure for six days, and
when removed from the cylinder neither the Portlands or Iron Ore
cements appeared harmed except cement B_3 which went to pieces. The
reason for the disintegration of this cement is unexplainable ex-
cept that it was not clinkered properly. The boiling test, however,
showed a good cement.

As the crushing strength tests of the Portlands show,
there seemed to be no weakening of them by being in the salt solu-
tion. Also the strength of the Portlands seems to average higher
than the Iron Ore cements.

Five cubes of each cement of Series "C" was then placed
into the cylinder with a set of Portland cubes made the same time.
These were kept under pressure for eight days. The results of this
series were quite different as four of the five cement cubes were
badly cracked and had begun to swell. C_2, C_3 , and C_4 showed no
signs of disintegration, but C_1 was cracked and swollen badly. This
cement as the "A" Series did not stand the boiling test, and such
an action could be expected from it when under the extreme conditions

in the pressure cylinder. The crushing strenghs of C_2 , C_3 , and C_4 averaged lower than the "B" Series, C_2 was so soft that disintegration had evidently set in.

Results of Six Hour Boiling Test
made after 60 hours in moist chamber.

Number		Appearance after Sea Water Test.
A_1	Good	Cracked.
A_2	Cracked plate.	"
A_3	Came loose from plate and showed some expansion.	"
A_4	Same as A_3.	"
B_1	Good	Sound.
B_2	"	"
B_3	"	Went to pieces.
B_4	"	Sound.
C_1	Came loose from plate, warped.	Cracked and swollen.
C_2	Good.	Sound.
C_3	Good.	"
C_4	"	"

Crushing Strength of Cements.

No.	Cross-sectional Area.	Strength	Strength per in sq.	Average
	P_1 = Portlands in fresh water 3 weeks.			
P_1	1.08 sq.in.	7680	7100	
P_1	0.975 " "	4780	4900	
P_1	1.06 " "	6650	6280	
P_1	1.045 " "	5650	4910	
P_1	1.105 " "	7750	7020	6042
	P_2 = Portland cement in fresh water 4 weeks.			
P_2	0.97 " "	7850	8700	
P_2	0.95	6620	6970	
P_2	0.97	7730	7960	7876
	P = Portland cements treated with salt solution under pressure with Series "B" of the Iron Ore Cements.			
P	0.97	5420	5590	
P	1.25	4860	3890 [2]	
P	1.025	7650	7470	
P	0.98	7330	7470	
P	1.01	7200	7150	6920

(Continued)

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[2] Signifies not calculated in average.

No	Cross-sectional Area.		Strength	Strength per in sq.	Average
	Iron Ore Cement in salt solution under pressure cylinder 6 days.				
B_1	1.035	sq.in.	5810	5620	
B_1	1.075	" "	6720	6250	
B_1	1.035	" "	5120	4915	
B_1	1.06	" "	4740	4460	
B_1	1.045	" "	5200	4860	5241
B_2	1.105	" "	7170	6500	
B_2	1.02	" "	6620	6000	
B_2	1.055	" "	7500	7100	
B_2	1.115	" "	8430	7550	
B_2	1.125	" "	6680	5930	6616
B_4	1.09	" "	4480	4120	
B_4	1.075	" "	5180	4820	
B_4	1.10	" "	5000	4540	
B_4	1.06	" "	6610	6240	
B_4	1.12	" "	6000	5350	5014
C_2	1.025	" "	4200	4080	
C_2	1.03	" "	5400	4360	
C_2	1.025	" "	6320	6160	
C_2	1.1	" "	5850	5310	
C_2	1.04	" "	4850	4660	4914
C_3	1.05	" "	2280	2190	
C_3	0.97	" "	1580	1660	
C_3	1.1	" "	2640	2400	
C_3	1.00	" "	1820	1880	
C_3	1.01	" "	2500	2480	2110

No	Cross-sectional Area.		Strength	Strength per in. sq.	Average
C_4	1.07	sq.in.	3220	3000	
C_4	1.07	" "	6630	6150[3]	
C_4	1.06	" "	3630	3330	
C_4	1.07	" "	5140	4800	
C_4	1.04	" "	4050	3900	3757
			o		
Portlands in Cylinder 7 days with Series "C".					
P	0.99	" "	3000	3030	
P	0.97	" "	6720	6930[2]	
				[2]Only unaffected Portland cement cube.	

[3]Signifies not calculated in average.

Conclusions.

As the time for this investigation was limited, further investigating could not be done, and the conclusions which may be drawn from these results are limited. This much may be said, however:
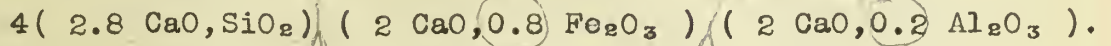
First: The amount of lime or silicate of lime ought to be less when Fe_2O_3 alone is used in place of Al_2O_3 as the lowest ratio of Series "A" 5.1 was the only one which stood the boiling test. Series "B" showed that the limits gave good cements throughout, neglecting B_3 which must have disintegrated due to some other cause. Series "C" showed that the lime and silica required increased as the lower ratio 5.44 disintegrated and the higher ratios were good. To sum this up, when all iron is used the $R_2O_3 : SiO_2$ ratio

should be below 5.1 when .175 to .2 mols Al_2O_3 is used with .825 to 0.8 mols of Fe_2O_3 the ratios lie between 5.1 to 7.22. If .36 to .4 mol of Al_2O_3 the ratio must be 5.8 or greater. This but a suggestion and will require further experimenting to show it definitely.

Second:that cements with large amounts of Fe_2O_3 will stand saline solutions better than cements containing Al_2O_3 was shown in the test of Series "C" where the Portlands were actually disintegrated and the iron cements stood the same test.

Third: The results seem to suggest that if the amount of lime was reduced lower than 2.8 CaO in Bleininger's formula that better strength could be obtained. There was found in the bottom of the vessel, after each trial in the cylinder, a heavy muddy deposit which was principally hydrated lime and which appeared to have been leached from the cubes. This reduction of the amount of lime may not need to be as much as the results suggest if the raw materials were clay and limestone in place of pure whiting, $Al_2(OH)$, and flint. All of the iron cements would have stood the tests better if they had been allowed to stand in the atmosphere and age, thus giving the lime time to become calcium carbonate. The Portland cement, which these cements were tested against, was one of the best cements on the market. It tested as follows: Initial set, 3 hours; final set 4 1/2 hours; tensile strength of neat cement after seven days, 679 pounds; after 28 days, 774 pounds; and its crushing strength is shown in the above tables. This cement had also aged several months in the laboratory and was in the best of condition to stand accelerated tests. The percent of lime given by Mr. Wm. Michaelis is 63.5% with a small amount of magnesia, MgO, 1.5%. The

cements made for this thesis are all above 66%, this is only
another evidence that these conclusions are correct and the follow-
ing formula is suggested as the center of a series of cements for
further experimenting:

$$4(\ 2.8\ CaO,SiO_2\ )\ (\ 2\ CaO,0.8\ Fe_2O_3\ )\ (\ 2\ CaO,0.2\ Al_2O_3\ ).$$

from this vary both the amount of SiO_2 and CaO.

PLATE I

$(3CaO, SiO_2)$

$(2CaO, Al_2O_3)$

$(2CaO, Fe_2O_3)$

100 0

90 10

80 20

70 30

60 40

50 50

40 60

30 70

20 80

10 90

0 100

100 11   90 10   12 10   80 9   13   36 20   14   29   31 30   70 8   15   28   32   47 40   60 7   16   27   33   44   46 50   50 6   17   26   34   43   47   56 60   40 5   18   25   35   42   48   57 10   30 4   19   36   41   49   55   58   63 80   20 3   24   37   40   50   53   54   62   64 90   10 2   23   38 02   39 09   51 05   52 04   60 30   59   61 20   65 10   21 06   22 08   0 00

PLATE 2

PLATE 3

Salt
Solution

DRAIN
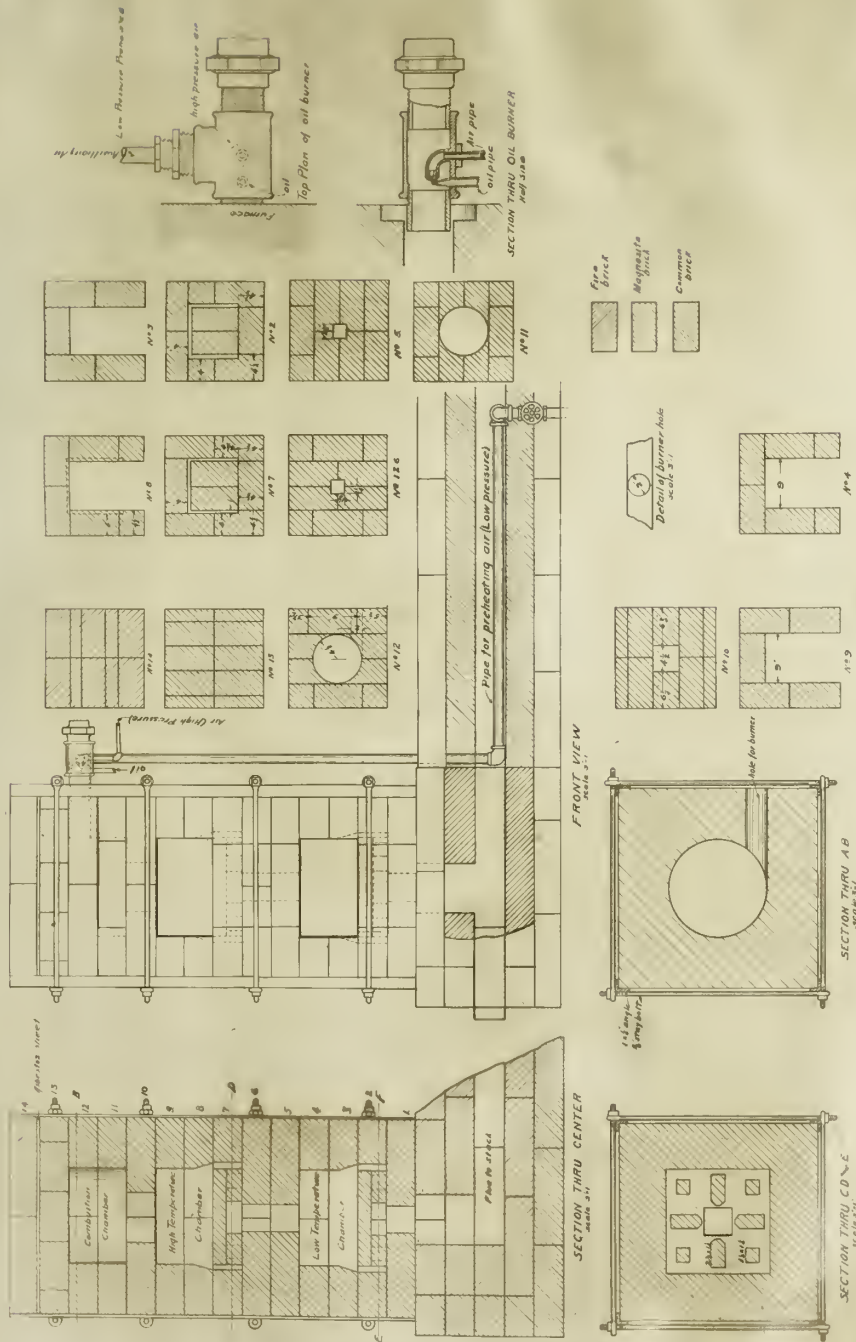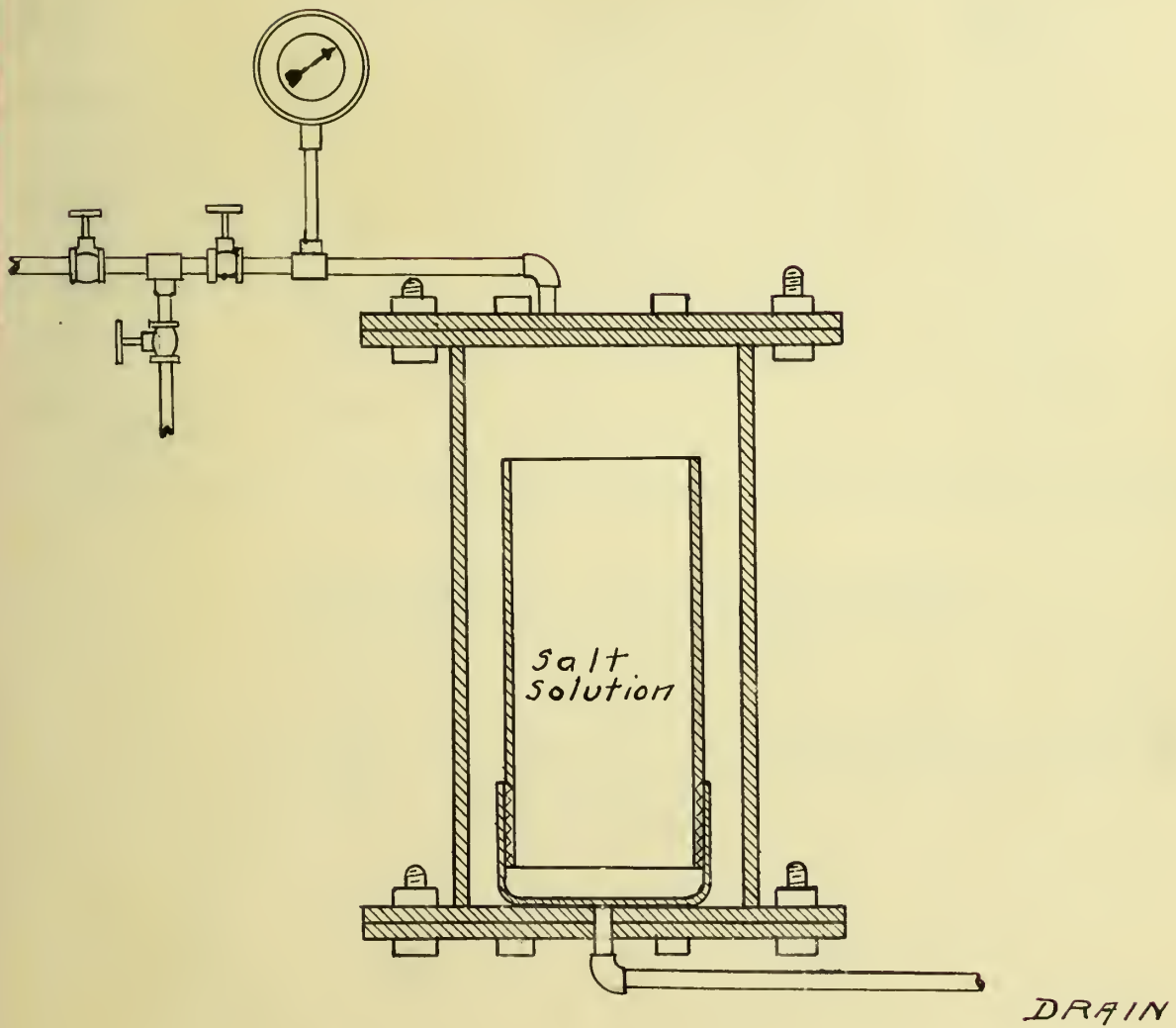
HIGH PRESSURE CYLINDER

ANALYSIS OF SEA WATER[2]

Salt	Percent of Salt.	Ten times per-cent of salt.	Total for 12 liters of water.
NaCl	77.75	-------	342.10
$MgCl_2$	10.87	108.7	478.28
$MgSO_4$	4.73	47.3	208.12
$CaSO_4$	3.60	36.0	158.40
K_2SO_4	2.46	-------	10.80
MgBr	0.217	-------	0.93
$CaHCO_3$	0.345	-------	1.62

37.3 parts per thousand parts water.

100 parts = 2700 parts water.

$$\frac{12000}{2700} = 4.4 \text{ factor times } \% \text{ of salt} = \text{quanity per 12}$$
liters of water.

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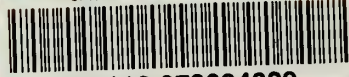Dr. Michaelis -- Tone Industrie Zeitung, 1896, p, 838.

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